

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
7 March 2002 (07.03.2002)

PCT

(10) International Publication Number
WO 02/18487 A1

- (51) International Patent Classification⁷: C08L 23/04, (74) Agent: DORRESTIJN, Antoon; DSM Patents & Trade-
23/10, 23/16, C08K 5/00, C08L 21/00 marks, P.O. Box 9, NL-6160 MA Geleen (NL).
- (21) International Application Number: PCT/NL01/00619 (81) Designated States (*national*): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
(22) International Filing Date: 22 August 2001 (22.08.2001) CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
(25) Filing Language: English LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NO, NZ, PH, PL, PT, RO, RU, SD, SE, SG, SI,
(26) Publication Language: English SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU,
ZA, ZW.
- (30) Priority Data: 30 August 2000 (30.08.2000) NL (84) Designated States (*regional*): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European
(71) Applicant (*for all designated States except US*): DSM N.V. patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,
[NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL). IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF,
CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD,
TG).
- (72) Inventors; and
(75) Inventors/Applicants (*for US only*): SCHMIDT, Ange-
lika [DE/NL]; Holstierbeek 26, NL-6166 JR Sittard (NL).
SOLIMAN, Maria [NL/NL]; Aan de Linde 11, NL-6118
AN Nieuwstadt (NL). TACX, Jacobus, Christiaus,
Josephus, Franciscus [NL/NL]; Bisschop Boermansstraat
60, NL-6041 XN Roermond (NL). WILLEMS, Edwin
[NL/NL]; Rolandsweg 8, NL-6136 BV Sittard (NL).

Published:
— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 02/18487 A1

(54) Title: THERMOPLASTIC ELASTOMER WITH IMPROVED LOW TEMPERATURE PROPERTIES

(57) Abstract: Thermoplastic elastomer composition comprising: a) at least one thermoplastic polyolefin polymer b) at least one dynamically vulcanized rubber in which the quantity of a) is 10-90 % by weight and the quantity of b) is 90-10% by weight relative to the total quantity of thermoplastic polyolefin polymer and rubber and c) 1-250 parts of oil per 100 parts of rubber, in which the oil comprises an isoparaffinic oil.

THERMOPLASTIC ELASTOMER WITH IMPROVED LOW TEMPERATURE PROPERTIES

5

The invention relates to a thermoplastic elastomer composition

comprising:

- a) at least one thermoplastic polyolefinic polymer
b) at least one dynamically vulcanized rubber
10 in which the quantity of a) is 10-90 % by weight and the quantity of
b) is 90-10 % by weight relative to the total quantity of thermoplastic
polyolefinic polymer and rubber, and
c) 1-250 parts of oil per 100 parts of rubber.

Such thermoplastic elastomer compositions are known from
15 US-A-4311628. The thermoplastic elastomer compositions comprise a blend of a
thermoplastic polyolefinic polymer, a dynamically vulcanized rubber and mineral
type of extender oil such as aromatic, naphthalenic or paraffinic oil or mixtures
thereof. A drawback of the described thermoplastic elastomer compositions is the
fact that they have poor low temperature impact properties, especially for high
20 hardness compositions. This poor low temperature impact performance can be
ascribed to the presence of the thermoplastic polyolefinic polymer in the
thermoplastic elastomer composition. The higher the quantity of thermoplastic
polyolefinic polymer the worse the low temperature impact performance.

The object of the present invention is to completely or largely
25 eliminate the stated drawback.

This object is achieved according to the invention by the
thermoplastic elastomer composition comprising an isoparaffinic oil.

Surprisingly, it has been found that the thermoplastic elastomer
compositions according to the invention show very good low temperature impact
30 properties. A further advantage is that the thermoplastic elastomer compositions
show a good UV resistance. Moreover the thermoplastic elastomer compositions
have a low fogging value which makes them suitable for use in for example
automotive interior applications.

From EP-A-315363 it is known to prepare EPDM compositions
35 comprising a polyalphaolefinic oil. However, EP-A-315363 is silent about the
impact resistance of the EPDM compositions and does not mention nor suggest
thermoplastic elastomers.

Thermoplastic elastomer compositions which comprise dynamically vulcanized rubber are known per se and are described in general terms in "Handbook of Thermoplastic Elastomers, by B.M. Walker/C.P. Rader, chapter 4, Elastomeric Alloy Thermoplastic Vulcanisates, Van Nostrand Reinhold, New York, 1988".

Suitable thermoplastic polyolefinic polymers in the thermoplastic elastomer composition according to the invention are the thermoplastic polyolefins known per se. Examples of these thermoplastic polyolefins are polyethylene, polypropylene, random or block copolymers of polypropylene, polybutene, polymethylpentene or copolymers of ethylene with alphaolefins such as a copolymer of ethylene and 1-butene or ethylene and 1-octene.

Preferably the thermoplastic elastomer composition comprises polyethylene or polypropylene as thermoplastic polyolefin.

A suitable quantity of the thermoplastic polyolefinic polymer in the thermoplastic elastomer composition according to the invention is between 10-90 % by weight relative to the total quantity of thermoplastic polyolefinic polymer and rubber. Preferably the quantity of the thermoplastic, polyolefinic polymer is between 20-85 % by weight relative to the total quantity of thermoplastic polyolefinic polymer and rubber.

Suitable rubbers in the thermoplastic elastomer composition according to the invention are rubbers that can be dynamically vulcanized. During the preparation of the thermoplastic elastomer composition, the rubber and the thermoplastic polyolefinic polymer are heated and mixed, with the rubber being vulcanized. Such vulcanization is referred to as dynamic vulcanization because it takes place during the melt mixing of the thermoplastic elastomer composition. The dynamically vulcanized rubber in the thermoplastic elastomer composition is dispersed in a matrix of the thermoplastic polyolefinic polymer. Examples of suitable rubbers are the following rubbers or a mixture thereof: SBR (styrene-butadiene rubber, copolymer of styrene and butadiene), NBR (nitrile rubber, copolymer of butadiene and acrylonitrile), IIR (butyl rubber, copolymer of isobutene and isoprene) or BR (butadiene rubber). Other examples of suitable rubbers are styrene-containing block copolymers: SBS (Styrene butadiene block copolymer), SEBS (styrene ethylene/butadiene styrene block copolymer), SIPS (styrene isoprene block copolymer).

Yet more examples of suitable rubbers are olefinic rubbers; these are rubbers based on homopolymers and copolymers of polyolefinic polymers. Examples of these are EPDM rubber (copolymer of ethylene, propylene and a third monomer) or a mixture of EPM rubber (copolymer of ethylene and propylene) and EPDM rubber.

5 Preferably, the dynamically vulcanized rubber in the thermoplastic elastomer composition according to the invention is an olefinic rubber. It is especially preferred for the dynamically vulcanized rubber in the thermoplastic elastomer composition according to the invention to be a copolymer of ethylene, propylene and a third monomer (EPDM) or a mixture of EPDM and a
10 copolymer of ethylene and propylene (EP) or a copolymer of ethylene with a higher alphaolefin or a mixture of EPDM, EP, styrene butadiene block copolymer (SBS) and/or styrene ethylene/butadiene styrene block copolymer (SEBS).

A suitable quantity of the dynamically vulcanized rubber in the
15 thermoplastic elastomer composition according to the invention is between 90-10 % by weight relative to the total quantity of thermoplastic polyolefinic polymer and rubber. Preferably, the quantity of the dynamically vulcanized rubber is between 80-15 % by weight relative to the total quantity of thermoplastic polyolefinic polymer and rubber.

20 The thermoplastic elastomer composition according to the invention comprises between 1-250 parts of oil per 100 parts of rubber. Preferably the quantity of oil is between 50-200 parts per 100 parts of rubber. It is especially preferred for the thermoplastic elastomer composition to comprise between 100-160 parts of oil per 100 parts of rubber.

25 Any known isoparaffinic oil may be used in the thermoplastic elastomer composition according to the invention. Isoparaffinic oil is also known as polyalphaolefinic oil which is a colourless, odourless, isoparaffinic, synthetic fluid of high purity composed of hydrogenated oligomers. Polyalphaolefinic oil comprises
30 oligomers of alphaolefins which contain alphaolefin monomer units of at least 3 carbon atoms. Exemplary oligomers of alphaolefins contain monomer units with from 6 to 12 carbon atoms. Preferred oligomers of alphaolefins contain monomers with 10 carbon atoms. Preferably, use is made of isoparaffinic oil with a weight-average molecular weight of 1000 g/mole or lower. Isoparaffinic oil with a weight-average molecular weight of between 250 and 700 g/mole is especially preferred.
35 Isoparaffinic oil with a weight-average molecular weight of between 400 and 600

g/mole is even more preferred.

In the thermoplastic elastomer composition according to the invention there may be present, besides the isoparaffinic oil, for example one or more other oils. Suitable oils that may be used in addition to the isoparaffinic oil are for
5 example mineral paraffinic oil, naphthenic oil, aromatic oil or mixtures thereof. Preferably a highly hydrogenated oil is used in which the concentration of aromatic compounds is preferably less than 4 wt.% and the concentration of polar compounds is less than 0.3 wt.%. An example of such oil is PennzUltra (TM) 1199, supplied by Pennzoil in the United States of America. The quantity of
10 isoparaffinic oil in the thermoplastic elastomer composition according to the invention is preferably at least 25 % by weight of the total quantity of oil. More preferably the thermoplastic elastomer composition comprises at least 50 % by weight isoparaffinic oil relative to the total quantity of oil.

In addition, the thermoplastic elastomer composition according
15 to the invention may comprise customary and known additives. Examples of such additives are fillers, reinforcing agents, colourants and stabilizers.

A process for producing the thermoplastic elastomer compositions which comprise dynamically vulcanized rubber is known per se and is described in general terms in US-A-4,311,628. That process is suitable for
20 producing the thermoplastic elastomer composition according to the invention. A suitable process comprises for example mixing and heating the thermoplastic polyolefinic polymer with the rubber, the vulcanising agent and additives, if any, at a temperature above the melting point of the thermoplastic polyolefinic polymer in which the rubber is dynamically vulcanized and the thermoplastic elastomer
25 composition is formed.

The point in time at which the oil that is present in the thermoplastic elastomer composition according to the invention is metered is not critical. In the process, the oil is added for example before or after the dynamic vulcanization of the rubber. It is also possible for the oil to be added partly before
30 and partly after the dynamic vulcanization of the rubber. It is also possible for the rubber used to be pre-mixed with the desired quantity of oil or a proportion thereof.

Suitable vulcanizing agents for the thermoplastic elastomer composition according to the invention are the vulcanizing agents known per se
35 for vulcanizing the stated rubbers. Examples of suitable vulcanizing agents are

phenol resins, peroxide, alkoxysilane and hydrosilane compounds.

The above-mentioned process for producing the thermoplastic elastomer composition according to the invention may be carried out with the aid of items of equipment known per se. Examples of suitable items of equipment are
5 extruders, mixers and kneaders.

The thermoplastic elastomer composition according to the invention may be used in moulded articles which are applied in cars, equipment and constructions. Examples hereof are airbag covers, fuel lines, hoses, dashboard foils, door panels, spoilers, mud flaps, seals, boots, strips and exterior
10 trim.

The invention is elucidated with reference to the following examples, without being limited thereto.

Example I

The following materials were metered to a ZSK40 40-mm twin-
15 screw extruder.

100 parts by weight of EPDM rubber (Keltan® 509 supplied by DSM)

250 parts by weight of polypropylene (Stamylan® P13E10 supplied by DSM)

10 parts by weight of talc (of Sigma-Aldrich)

20 5 parts by weight of zinc oxide (ZnO supplied by Sigma-Aldrich)

1 part by weight of zinc stearate (supplied by Sigma-Aldrich)

1.5 parts by weight of phenol resin (SP1045 supplied by Schenectady)

1 part by weight of tin(II)chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ supplied by Aldrich)

1.5 parts by weight of antioxidant (Irganox® 1076 supplied by Ciba Geigy)

25 140 parts by weight of isoparaffinic oil (Nexbase® 2006 supplied by Neste).

The extruder heating system had been adjusted to a temperature of 205°C.

The metered materials were mixed, in which process the EPDM rubber was dynamically vulcanized. Thermoplastic elastomer composition I was obtained in the process.

30 Test specimens were prepared from thermoplastic elastomer I and their properties were measured according to the test standards stated in Table 1.

Table 1

Property	Test standard
Hardness	DIN 53505
Tensile strength	ISO 37
Modulus 100%	ISO 37
Modulus 300%	ISO 37
Elongation at break	ISO 37
Compression set, 70 h/23°C	ISO 815/B
Compression set, 22 h/70°C	ISO 815/B
Notched Izod -45°C	ISO 180/4 A
Fogging	DIN 75201/B
UV test surface	P.S.A. D47 1431/-G (1992)

The results of the performed tests are shown in Table 3.

5 Comparative experiment A

The isoparaffinic oil of Example I was replaced by an equal quantity of mineral paraffinic oil, Sunpar®150, from Sun Oil.

The applied quantities of the various components are stated in Table 2.

10 The properties of thermoplastic elastomer A were determined according to the tests in Table 1. The results are stated in Table 3.

Example II

A proportion of the isoparaffinic oil, 50 parts by weight, of Example I was replaced by an equal quantity of a mineral paraffinic oil,

15 Sunpar®150, from Sun Oil.

The applied quantities of the various components are stated in Table 2.

The properties of thermoplastic elastomer II were determined according to the tests of Table 1. The results are stated in Table 3.

20 Example III

The oil of example I was replaced by 60 parts by weight of isoparaffinic oil (Nexbase®2004 from Neste) and 100 parts by weight of Sunpar®150.

The quantity polypropylene was lowered to 40 parts by weight.

The quantity of talc was increased to 30 parts by weight and the quantity of phenol resin was increased to 3.5 parts by weight.

The applied quantities of the various components are stated in Table 2.

- 5 The properties of thermoplastic elastomer III were determined according to the tests of Table 1. The results are stated in Table 3.

Table 2

Composition of the examples and comparative experiment A.

Quantities are expressed as parts by weight.

Material	I	A	II	III
Keltan @ 509	100	100	100	100
Stamylan® P13E10	250	250	250	40
Talc	10	10	10	30
ZnO	5	5	5	5
Zinc stearate	1	1	1	1
SP1045	1.5	1.5	1.5	3.5
SnCl ₂ ·2H ₂ O	1	1	1	1
Irganox® 1076	1.5	1.5	1.5	1.5
Nexbase® 2006	140		90	
Nexbase® 2004				60
Sunpar® 150		140	50	100

Table 3. Test results

Test	Unit	I	A	II	III
Hardness	Shore A or	42 D	43D	43 D	58 A
	Shore D				
Tensile strength	MPa	15.0	15.1	15.1	3.8
Modulus 100%	MPa	11.1	11.1	11.0	2.2
Modulus 300%	MPa	11.8	12	11.9	3.9
Elongation at break	%	623	643	604	310
Compression set, 70 h/23°C	%	41	43	42	20
Compression set, 22 h/70°C	%	56	58	58	29
Notched Izod -45°C	-	Tough fracture	Brittle fracture	Tough fracture	Tough fracture
Notched Izod energy	KJ/m2	64	8	56	59
Fogging	mg	1.6	1.5	1.2	1.0
UV test surface	-	No	No	No	None
		Change	change	Change	Change

Analysis of the test results in Table 3 indicate that thermoplastic elastomer compositions comprising isoparaffinic oil show improved low temperature impact properties in comparison with thermoplastic elastomer compositions comprising only mineral paraffinic oil.

CLAIMS

1. Thermoplastic elastomer composition comprising:
 - a) at least one thermoplastic polyolefinic polymer
 - 5 b) at least one dynamically vulcanized rubber
in which the quantity of a) is 10-90 % by weight and the quantity of b)
is 90-10 % by weight relative to the total quantity of thermoplastic
polyolefinic polymer and rubber and
 - c) 1-250 parts of oil per 100 parts of rubber,
10 characterised in that the thermoplastic elastomer composition comprises
an isoparaffinic oil.
2. Thermoplastic elastomer composition according to Claim 1, characterized
in that the isoparaffinic oil has a weight average molecular weight of 1000
g/mole or lower.
- 15 3. Thermoplastic elastomer composition according to Claim 2,
characterized in that the isoparaffinic oil has a weight average molecular
weight of between 250 and 700 g/mole.
4. Thermoplastic elastomer composition according to Claim 3, characterized
in that the isoparaffinic oil has a weight average molecular weight of
20 between 400 and 600 g/mole.
5. Thermoplastic elastomer composition according to Claim 1, characterized
in that the quantity of oil is between 50-200 parts per 100 parts of rubber.
6. Thermoplastic elastomer composition according to Claim 5, characterized
in that the quantity of oil is between 100-160 parts per 100 parts of
25 rubber.
7. Thermoplastic elastomer composition according to Claim 1, characterised
in that the thermoplastic polyolefinic polymer is polyethylene or
polypropylene.
8. Thermoplastic elastomer composition according to Claim 1, characterized
in that the dynamically vulcanized rubber is an olefinic rubber.
- 30 9. Thermoplastic elastomer composition according to Claim 8, characterized
in that the dynamically vulcanized rubber is a copolymer of ethylene,
propylene and a third monomer (EPDM) or a mixture of EPDM and a
copolymer of ethylene and propylene (EPM) or a copolymer of ethylene
35 with a higher alphaolefin or a mixture of EPDM, EPM, styrene butadiene

block copolymer (SBS) and/or styrene ethylene/butadiene styrene block copolymer (SEBS).

10. Moulded article containing a thermoplastic elastomer composition according to Claims 1-9.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/NL 01/00619

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08L23/04 C08L23/10 C08L23/16 C08K5/00 C08L21/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08L C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
PAJ, EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 98 44041 A (WICKSTROEM GOERAN ;UPOFLOOR OY (FI); KARTTUNEN MIKKO (FI); PELTONE) 8 October 1998 (1998-10-08) abstract; claims 1-12 page 3, line 31-39 page 5, line 1-8,19-23,35 page 8, line 25 -page 9, line 7 page 13; table 3	1-9
Y	EP 0 742 268 A (ADVANCED ELASTOMER SYSTEMS) 13 November 1996 (1996-11-13) abstract; claims 1-17 page 2, line 50 page 3, line 16,45 page 4, line 1,50 page 5, line 1-5	1-10

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- *G* document member of the same patent family

Date of the actual completion of the international search

29 November 2001

Date of mailing of the international search report

19/12/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Bergmans, K

INTERNATIONAL SEARCH REPORT

Int. Application No.
PCT/NL 01/00619

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		Relevant to claim No.
Category *	Citation of document, with indication, where appropriate, of the relevant passages	
Y	US 4 645 791 A (THEODORE ARES N ET AL) 24 February 1987 (1987-02-24) abstract; claims 1-18 column 2, line 51-53, 59-61 column 3, line 19, 42, 54-67 column 4, line 2-6, 15-26 column 5, line 31	1-10

INTERNATIONAL SEARCH REPORT

 International Application No
 PCT/NL 01/00619

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9844041	A	08-10-1998	FI 971338 A	03-10-1998
			AU 6733698 A	22-10-1998
			WO 9844041 A1	08-10-1998
EP 0742268	A	13-11-1996	US 5574105 A	12-11-1996
			AU 697634 B2	15-10-1998
			AU 5221696 A	21-11-1996
			BR 9602206 A	07-04-1998
			CA 2174908 A1	13-11-1996
			CN 1139686 A	08-01-1997
			DE 69611395 D1	08-02-2001
			DE 69611395 T2	23-08-2001
			EP 0742268 A2	13-11-1996
			ES 2153912 T3	16-03-2001
			JP 9025370 A	28-01-1997
US 4645791	A	24-02-1987	CA 1285348 A1	25-06-1991
			EP 0210733 A2	04-02-1987
			JP 61296047 A	26-12-1986